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SPECIFICATION

1. Title of the Invention:

OPTICAL INFORMATION RECORDING CARRIER

2. Claims:

1. An optical information recording carrier comprising a substrate and an information recording material layer formed over the substrate, said layer being evaporated, vaporized, melted, or reacted by laser light applied thereto to record information, wherein said information recording material layer comprises a composite layer of a metal and an oxide and has a semi-metal layer made of a carbon layer, a silicon layer, or a boron layer and having a high melting point at least on one side of said information recording material layer.

2. An optical information recording carrier as claimed in claim 1, wherein the oxide in the information recording material layer contains one oxide selected from the group consisting of SnO_2, Fe_2O_3, Sb_2O_5, MnO_2, V_2O_5, and oxide containing

at least one or more of these oxides.

3. An optical information recording carrier as claimed in claim 1, wherein the metal in the information recording material layer contains one metal selected from the group consisting of Cr, Mg, Ti, Zr, V, Nb, Ta, Mo, W, Mn, Fe, Co, Ni, Cu, Ag, Au, Zn, Al, In, Sn, Pb, Sb, and Bi, or an alloy containing at least one or more metals selected from the group of the metals described above.

4. An optical information recording carrier as claimed in claim 1, wherein the composite layer of the metal and the oxide for the information recording material layer has a structure in which metal particles are diffused in the oxide.

5. An optical information recording carrier as claimed in claim 1, wherein the composite layer of the metal and the oxide in the information recording material layer has a structure in which a plurality of metal layers and a plurality of oxide layers are laminated in a multi-layer.

6. An optical information recording carrier as claimed in claim 1, wherein the thickness of the information recording material layer ranges from 20 nm to 400 nm.

7. An optical information recording carrier as claimed in claim 1, wherein the thickness of the semi-metal layer having a high melting point ranges from 10 nm to 200 nm.

8. An optical information recording carrier as claimed in claim 1, wherein the total thickness of the information

recording material layer and the semi-metal layer having a high melting point ranges from 30 nm to 600 nm.

9. An optical information recording carrier as claimed in claim 1, wherein at least one or more optical information recording structural layers constituted by two layers of the information recording material layer and the semi-metal layer having a high melting point which are laminated in sequence is formed over the substrate.

10. An optical information recording carrier as claimed in claim 9, wherein at least one or more optical information recording structural layers constituted by two layers of a composite layer of Cr and SnO_2 and a C layer which are laminated in sequence is formed over the substrate.

11. An optical information recording carrier as claimed in claim 1, wherein an optical information recording structural layer constituted by three layers of a first semi-metal layer having a high melting point, an information recording material layer, and a second semi-metal layer having a high melting point which are laminated in sequence is formed over the substrate.

12. An optical information recording carrier as claimed in claim 11, wherein an optical information recording structural layer constituted by three layers of a first C layer, a composite layer of Cr and SnO_2, and a second C layer which are laminated in sequence is formed over the substrate.

3. Detailed Description of the Invention

The present invention relates to an optical information recording carrier which is evaporated, vaporized, melted, or reacted by laser light applied thereto to record information.

Laser light is applied to the optical information recording carrier rotating at high speeds to record information bits in the recording thin film of the optical information recording carrier and the recorded information can be read out by applying laser light thereto. It is possible to conduct the real-time recording and reproducing of the information and to get random access at high speeds. There are two modes for forming the information bits in the optical information recording thin film, that is, a heat recording mode and a mode of changing the optical characteristics of substance, for example, a refractive index or a reflection factor. In the heat recording mode, thermal energy with high energy density, such as laser light, is converged on a spot and is applied to the optical recording thin film to evaporate, vaporize, melt, or diffuse a part of the thin film, whereby a part of the thin film is removed or deformed to form a small pit thereon. The optical information recording thin film of the heat recording mode is required to have the following characteristics: the thin film has a large absorption coefficient of light and a low melting point so that the thin film is easily effectively heated, evaporated, vaporized, or melted, and is removed when the laser light is applied thereto; it has a suitable thermal

conductivity and is small in energy required to write information; it has no grain boundary or a sufficiently small gain size compared to a writing pit diameter so as to increase a readout S/N ratio; it is shaped not in an island but in a uniform film; and it is highly stable for a long time. A film made of Te which has a low melting point, a high light absorption factor, and a suitable thermal conductivity, or a film containing Te as a major constituent has been known as the optical information recording layer satisfying such requirements, but the Te-based film has a problem that it is deadly poisonous. Although there are Bi, In, and Sn as materials for the optical information recording layer, each of which is alternative to Te and is weakly poisonous and has a low melting point, they have the following drawbacks: they can not produce a good pit shape because they can not provide a thin continuous uniform film and because they are larger in thermal conductivity than Te; they have a low S/N ratio; they are apt to oxidize and are low in stability and inferior in durability at high temperatures and high humidities; and they are inferior in mechanical strength. A sandwich structure in which a metallic film having a low melting point such as Te, Bi, In, Sn, or the like is sandwiched between oxide films such as SiO_2 film, or a method of making Te, Bi, In, Sn, or the like into a cermet film has been proposed as a method of overcoming the above drawbacks. However, any method is not sufficient

from the viewpoint of a pit shape and durability.

The present invention has been achieved on the basis of the results of a research, and it is an object of the present invention to provide an optical information recording carrier which overcomes the above described drawbacks and has more excellent writing characteristics and durability. In accordance with one aspect of the present invention, there is provided an optical information recording carrier having an information recording layer which is formed on a substrate and which is evaporated, vaporized, chemically reacted by laser light applied thereto to record information, wherein the information recording material layer is made of a composite layer of metal and oxide and wherein a metal layer or a semi-metal layer, or a semiconductor layer including a carbon layer, a silicon layer, or a boron layer and having a high melting point (in the present invention, hereinafter referred to as a semi-metal layer having a high melting point) is formed on at least one surface of the information recording material layer.

The present invention will hereinafter be described further in detail with reference to the drawings.

As a substrate 1 of an optical information recording carrier 5 in accordance with the present invention, in the case where a passing light is used for readout, a transparent glass plate, or a sheet or a film which is made of polymer such as

poly(methyl methacrylate), poly (ethylene terephthalate), polypropylene, polycarbonate, poly (vinyl chloride), polyamide, polystyrene, or the like or polymer modified therefrom, or copolymer thereof, or a blend of these polymers or copolymers is used; and in the case where a reflection light is used for readout, a substrate made of above described material and having a reflective coat applied thereto, an aluminum plate, or an aluminum alloy plate is used.

An optical information recording structural layer 4 having a given number of layers of an information recording material layer 2 and a semi-metal layer 3 having a high melting point is formed on such a substrate 1. A composite layer of metal and oxide is used as the information recording material layer 2. As the oxide of the composite layer, SnO_2, Fe_2O_3, Sb_2O_5, MnO_2, V_2O_5 which can have some different oxidative states, or a combination of at least two or more of them, or a material containing one or more these metal oxides can be used. Also, as the metal of the above described composite layer, from the viewpoint of providing the layer with the capability of absorbing laser light, one metal selected from the group consisting of Cr, Mg, Ti, Zr, V, Nb, Ta, Mo, W, Mn, Fe, Co, Ni, Cu, Ag, Au, Zn, Al, In, Sn, Pb, Sb, and Bi, or an alloy containing at least one or more metals selected from the group described above can be used. In accordance with the present invention, a semi-metal layer 3 having a high melting point

and including one element selected from the group consisting of C (carbon) layer, Si (silicon) layer, and B (boron) layer is formed on at least one surface of the information recording material layer 2. The pit of the optical information recording structural layer 4 in accordance with the present invention is formed mainly by the phenomenon that the oxide layer is changed into another oxidative state by laser light applied thereto to produce gas and that the produced gas plastically deforms the semi-metal layer having a high melting point. As a matter of course, there is a possibility that the recording layer undergoes a slight change, but the change is a secondary one so long as a present writing power level (less than 10 mW) is used.

Therefore, it is preferable that the metal constituting the composite layer is made of a metal having a comparably high melting point so that it helps to absorb laser light and that it contributes to a reaction to some extent to resist melting and vaporizing by itself. From this point of view, among the metals described above, Cr, Mg, Ti, Zr, V, Mn, Fe, Co, Ni, Cu, and Al are good, and Cr is the best of all in terms of durability. Carbon, silicon, and boron are selected for the semi-metal layer having a high melting point because it is thought that since these elements have a high melting point, the interaction of these elements with the information recording material layer 2 is less than that of the oxide and that they are easily deformed.

In addition to this, the optical information recording structural layer in accordance with the present invention has the following features:

(a) If the thickness of the semi-metal layer having a high melting point is determined in a suitable range, the reflection factor of the optical information recording structural layer for the wavelength of the laser light can be reduced, which can greatly improve a writing sensitivity;

(b) An organic substance is thought to be used as another substance for generating gas when a laser is applied thereto, but the oxide used in the present invention is superior to the organic substance in long-term durability. Further, it is advantageous in a manufacturing cost to make the optical recording structural layer only of inorganic substances, as described in the present invention, because a production process is made simple;

(c) The metal such as Cr, Ti, or Zr, by itself, is larger in thermal conductivity and is much lower in writing sensitivity than Te, but a combination of the metal with the oxide is capable of adjusting the thermal conductivity or heat capacity.

The thickness of the information recording material layer 2 in accordance with the present invention is determined by the sensitivity, the size and the durability of a recording portion, and the like in writing by a laser, and suitably ranges, for example, from 20 nm to 400 nm, more preferably, from 40

nm to 250 nm. Also, the thickness of the semi-metal layer 3 having a high melting point made of such as C, Si, B, or the like is determined by the sensitivity, the durability and the like, and also depends on the wavelength of the laser and is determined so that a reflection factor for that wavelength is reduced to the minimum, and suitably ranges from 10 nm to 200 nm, more preferably, from 20 nm to 600 nm. Therefore, the thickness of the optical information recording structural layer 4 including the information recording material layer 2 and the semi-metal layer 3 having a high melting point suitably ranges from 30 nm to 600 nm, more preferably, from 60 nm to 350 nm.

The information recording material layer 2 in accordance with the present invention may be a composite layer, as shown in FIG. 4, in which metal particles are diffused in the oxide, or may be a composite layer, as shown in FIG. 5, in which oxide layers and metal layers are laminated in a multilayer, wherein each of the oxide layers and the metal layers has a thickness of 0.5 nm to 50 nm. In this respect, the latter composite layer has little effect on writing characteristics. Also, the latter composite layer is advantageous in production because each evaporation source can be controlled by itself.

In the present invention, as shown in FIG. 1, the optical information recording structural layer 4 may have a simple two-layer constitution comprising the information recording

material layer 2 and the semi-metal layer 3 having a high melting point which is formed on the information recording material layer 2, or as shown in FIG. 2, the optical information recording structural layer 4 may have a three-layer constitution in which the information recording material layer 2 is sandwiched between the two semi-metal layers 3 having a high melting point. Further, in the present invention, in the case where the optical information recording structural layer 4 may have the three-layer constitution, it is preferable that the semi-metal layers 3 having a high melting point sandwiching the information recording material layer 2 are made of the same kind of material in the technical aspect of forming a film, but the semi-metal layers 3 having a high melting point sandwiching the information recording material layer 2 may be made of different materials selected from the group consisting of the metals described above. Further, in the present invention, one or several layers of functional layers such as a reflection layer, an insulating layer, a protective layer, an undercoat layer, an alkali barrier layer, or the like, or several layers of a combination of various kinds of the functional layers can also be formed on the top surface or on the bottom surface of the optical information recording structural layer 4, or on the surface of the substrate opposite to the surface on which the optical information recording structural layer 4 is formed. For example, in order to increase

a change in reflection factor before and after the writing of data to the optical information recording carrier, it is possible to form the optical information recording carrier of five layers including a semi-metal layer having a high melting point/a recording material layer/a semi-metal layer having a high melting point/a thermally insulating layer/a reflection layer/a substrate (for example, a C layer/a composite layer of Cr and SnO_2/a C layer/a thermally insulating layer/an Al layer/a substrate) and to write and read data to and from the optical information recording structural layer side. Further, in order to write and read the data to and from the substrate side, it is also possible to form the optical information recording carrier of five layers including a reflection layer/a thermally insulating layer/a semi-metal layer having a high melting point/a recording material layer/a semi-metal layer having a high melting point/a substrate (for example, an Al layer/a thermally insulating layer/a C layer/a composite layer of Cr and SnO_2/a C layer/a substrate).

In the present invention, a method of forming the information recording layer and the semi-metal layer having a high melting point on the substrate is not particularly limited to a specific method, but various kinds of film-forming methods such as various kinds of vacuum evaporation methods, various kinds of sputtering methods, various kinds of ion plating methods can be employed.

The embodiments in accordance with the present invention will be described below.

(Embodiment 1)

A circular float glass substrate excellent in surface smoothness (diameter: 85 mm, thickness: 2 mm) was prepared and the surface thereof was ground with cerium oxide and then was cleaned with a commercially available neutral detergent and gauze and was sufficiently rinsed with city water, distilled water, and ethanol in this order, and then was dried with nitrogen. This substrate 10 was attached to a rotating substrate-supporting member 12 in a sputtering unit 11 shown in FIG. 6. Carbon targets 13, 18 placed on a stainless plate, a chromium target 15 placed on a stainless plate, and a tin oxide target 16 placed on a stainless plate were used as sputtering targets. To form layers, first, the substrate-supporting member 12 was set on a shutter 14 and a vacuum chamber 15 was evacuated to 10^{-7} Torr level and then a highly pure argon gas was introduced into the vacuum chamber to control pressure to 3×10^{-3} Torr. Carbon was sufficiently pre-sputtered and then the shutter 14 was opened and a coating was started with the substrate 10 being rotated. Electric power impressed on the target 13 was controlled such that the thickness of a carbon layer became about 200 Å. Next, the substrate-supporting member 12 was moved over a shutter 17 and then Cr and SnO_2 were sufficiently pre-sputtered and then the shutter 17 was opened

and Cr and SnO_2 were alternately laminated in many layers with the substrate 10 being rotated. Electric power impressed on the targets 15, 16 was controlled such that the thickness of one Cr layer amounted to about 10 Å and that the thickness of one SnO_2 layer amounted to about 20 Å. Finally, the substrate-supporting member 12 was moved over the shutter 19 and carbon was sufficiently pre-sputtered like the first process and then the shutter 19 was opened and a coating was performed with the substrate 10 being rotated. Electric power impressed on the target 18 was controlled such that the thickness of a carbon layer amounted to about 200 Å. The total thickness of a three-layer film (C layer/composite layer of Cr and SnO_2/C layer) produced in this manner was 2000 Å. The reflection factor of the three-layer film was 23 % and the absorption factor of laser light was 69 % for the wavelength of an He-Ne laser. Data were written on the optical information recording carrier with an He-Ne laser (writing power: 8 mW) to evaluate the writing performance thereof. As a result, a recording pattern was produced in a good shape. Also, even if this sample was placed in an atmosphere of high temperature and high humidity (60 °C, 95 % RH) for one week, there was no sign of change on the sample and its spectral characteristics were little changed.

(Embodiment 2)

As is the case with the embodiment 1, a substrate 10 was

cleaned and dried, and then a three-layer film made of a C layer, a composite layer of Cr and SnO_2, and a C layer was formed, as is the case with the embodiment 1. However, when the C layers were formed on both sides of the composite layer of Cr and SnO_2, the same electric power that was impressed in the embodiment 1 was impressed and a coating time was shorted to the half of that in the embodiment 1 to reduce the thickness of the C layer to about 100 Å. The total thickness of the three-layer film produced in this manner was 1825 Å. The reflection factor of the three-layer film was 28 % and the absorption factor of laser light was 60 % for the wavelength of a He-Ne laser. Data were written on the optical information recording carrier with a He-Ne laser (writing power: 8 mW) to evaluate the writing performance thereof. As a result, a recording pattern was produced in a good shape. Also, even if this sample was placed in a hot and humid atmosphere (60 °C, 95 % RH) for one week, there was no sign of change on the sample and its spectral characteristics were little changed.

(Embodiment 3)

As is the case with the embodiment 1, a substrate 10 was cleaned and dried and then was placed on a substrate-supporting member 12 and the substrate-supporting member 12 was set on a shutter 17. A vacuum chamber 15 was evacuated to 10^{-7} Torr level and then a highly pure argon gas was introduced into the vacuum chamber 15 to control pressure to 3×10^{-3} Torr. Cr and

SnO_2 were sufficiently pre-sputtered and then the shutter 17 was opened and Cr and SnO_2 were alternately laminated in many layers with the substrate 10 being rotated. Electric power impressed on targets 15, 16 was controlled such that the thickness of one Cr layer became about 10 Å and that the thickness of one SnO_2 layer became about 20 Å. Next, the substrate-supporting member 12 was moved over a shutter 19 and carbon was sufficiently pre-sputtered and then the shutter 19 was opened and a coating was performed with the substrate 10 being rotated. Electric power impressed on the target 18 was controlled such that the thickness of a carbon layer became about 200 Å. The total thickness of a two-layer film produced in this manner was 1835 Å. The reflection factor of the three-layer film was 22 % and the absorption factor of laser light was 74 % for the wavelength of an He-Ne laser. Data were written on the optical information recording carrier to evaluate the writing performance of the carrier, as is the case with embodiment 1. As a result, a recording pattern was produced in a good shape, and even if this sample was placed in an atmosphere of high temperature and high humidity (60 °C, 95 % RH) for one week, there was no sign of change on the sample.

(Embodiment 4)

In this embodiment, a Zr target was used instead of a Cr target and a three-layer film (C layer/composite layer of Zr and SnO_2/C layer) was formed according to the same procedures

as in the embodiment 1. The total thickness of the film produced in this manner was 2575 Å. The reflection factor of the three-layer film was 18 % and the absorption factor of laser light was 81 % for the wavelength of an He-Ne laser. Data were written on the optical information recording carrier to evaluate the writing performance of the carrier, as is the case with embodiments 1, 2, 3. As a result, a good recording pattern was obtained and there was almost no problem in durability.

The test results of the specimens obtained in the embodiments 1 to 4 will be shown in Table 1.

Table 1

		Light absorption factor (for wavelength of a He-Ne laser)	Shape of recorded pattern(writing power: 8 mW)	Durability (60 °C, 95 % RH , for one week)
1	Sample obtained in embodiment 1	69 %	good	not changed
2	Sample obtained in embodiment 2	60 %	good	not changed
3	Sample obtained in embodiment 3	74 %	good	not changed
4	Sample obtained in embodiment 4	81 %	good	not changed
5	Comparative example (Te single layer, thickness: 70 nm)	45 %	good	changed

As described above, the optical information recording structural layer of an optical information recording carrier in accordance with the present invention has the following excellent advantages: a high light absorption factor when laser light is applied thereto, small energy required to write data, easy writing, good recording pattern shape, good durability, and low toxicity.

4. Brief Description of the Drawings

FIGs. 1 to 3 show cross-sectional views of a part of an

optical information recording carrier in accordance with the present invention. FIGs. 4 and 5 show cross-sectional views of a part of the optical information recording material layer of the optical information recording carrier in accordance with the present invention. FIG. 6 is a schematic view of a device for manufacturing the optical information recording carrier in accordance with the present invention.

(Description of Reference Numerals)

1: substrate, 2: information recording material layer, 3: semi-metal layer having a high melting point, 4: optical information structural layer, 5: optical information recording carrier.

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(54) OPTICAL INFORMATION-RECORDING MEDIUM
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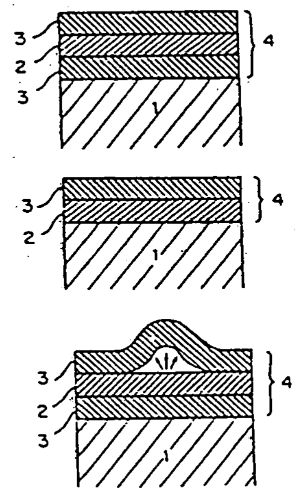

PURPOSE: To obtain an optical information-recording medium having excellent writing characteristics and durability, by a construction wherein an information-recording material layer consisting of a composite layer of a metal and an oxide, and a metal, semi-metal or semi-conductor layer consisting of a carbon layer, a silicon layer or a boron layer and having a high melting point is provided on at least one side of the information-recording material layer.

CONSTITUTION: An optical information-recording layer 4 comprising predetermined numbers of information-recording material layers 2 and high melting point semi-metal layers 3 is provided on a base 1. A composite layer of a metal and an oxide is used as the information-recording material layer 2. The semi-metal layer 3 selected from a C (carbon) layer, an Si (silicon) layer and a B (boron) layer is provided on at least one side of the layer 2. When the thickness of the layer 3 is selected from an appropriate range, a reflection-preventing effect is obtained, whereby the reflectivity at a laser wavelength of the optical information-recording layer 4 can be lowered, and the writing sensitivity can be thereby markedly enhanced.

DOC

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明　細　書

1.発明の名称

光情報記録担体

2.特許請求の範囲

(1) レーザー光を照射して蒸発，気化，溶融あるいは反応により情報の記録が行なえる情報記録材料層が基体上に形成されてなる光情報記録担体において，上記情報記録材料層が，金属と酸化物との複合層からなり，該情報記録材料層の少なくとも一方の側にC層，Si層，又はB層よりなる高融点半金属層が形成されていることを特徴とする光情報記録担体。

(2) 情報記録材料層の酸化物が，SnO_2，Fe_2O_3，Sb_2O_3，MoO_2，V_2O_5 又はこれらの少なくとも1種以上を含むものからなるものであることを特徴とする特許請求の範囲第1項記載の光情報記録担体。

(3) 情報記録材料層の金属がCr，Mg，Ti，Zr，V，Nb，Ta，Mo，W，Mn，Fe，Co，Ni，Cu，Ag，Au，Zn，Al，In，Sn，Pb，Sb 及び Bi からなる金属の中から選ばれた1つの金属，又は上記金属の少なくとも1つを成分とする合金からなるものであることを特徴とする特許請求の範囲第1項記載の光情報記録担体。

(4) 情報記録材料層の金属と酸化物の複合層は，酸化物中に金属が分散されている形態であることを特徴とする特許請求の範囲第1項記載の光情報記録担体。

(5) 情報記録材料層の金属と酸化物の複合層は金属層と酸化物層とが複数層積層された形態であることを特徴とする特許請求の範囲第1項記載の光情報記録担体。

(6) 情報記録材料層の厚さが20nm～400nmであることを特徴とする特許請求の範囲第1項記載の光情報記録担体。

(7) 高融点半金属層の厚さが10nm～200nmであることを特徴とする特許請求の範囲第1項記載の光情報記録担体。

(8) 情報記録材料層と高融点半金属層との合計

の厚さが30nm～600nmであることを特徴とする特許請求の範囲第1項記載の光情報記録担体。

(9) 基体上に情報記録材料層，高融点半金属層が順次積層されてなる2層構成の単位光情報記録構成層が少なくとも1単位以上形成されてなることを特徴とする特許請求の範囲第1項記載の光情報記録担体。

(10) 基体上にCrとSnO_2の混合層，C層が順次積層されてなる2層構成の光情報記録構成層が少なくとも1単位以上形成されてなることを特徴とする特許請求の範囲第9項記載の光情報記録担体。

(11) 基体上に第1の高融点半金属層，情報記録材料層，第2の高融点半金属層が順次積層されてなる3層構成の光情報記録構成層が形成されてなることを特徴とする特許請求の範囲第1項記載の光情報記録担体。

(10) 基体上に第1のC層，CrとSnO_2の混合層，第2のC層が順次積層されてなる3層構成の光情報記録構成層が形成されてなることを特徴とする特許請求の範囲第11項記載の光情報記録担体。

3.発明の詳細な説明

本発明は、レーザー光を照射して蒸発，気化，溶融あるいは反応等により情報の記録が行なえる光情報記録担体に関するものである。

光情報記録担体は、高速回転する該担体にレーザー光を照射して、その記録薄膜に情報ピットを記録し、この記録された情報はレーザー光の照射によって読み取られるものであり、現時記録再生，高速ランダム・アクセスが可能である。光情報記録薄膜への情報ピットの形成方法としては、レーザー光線などの光密度熱エネルギーをスポットに集束させて光情報記録薄膜に照射し、かかる薄膜の一部を蒸発，気化，溶融あるいは拡散により除去あるいは変形させてピット（小孔）を形成するヒート・モード記録方式と、物質の光学的特性、例えば屈折率や反射率を変化させる方式とがある。前者の方式の光情報記録薄膜としては、レーザー光の照射時において、かかる薄膜が容易に、かつ効果的に加熱されて蒸発，気化，溶融などにより除去される様に、薄膜材料の光の吸収係数が大きく、融点が低く、又、熱伝導性が適当で、書き込みに要するエネルギーが小さいこと，読み出しS/N比向上のため，粒界がないか、あるいは粒径が書き込みピット径に比べて十分小さいこと、島状とならず均一な膜が得られること，長期間の安定性が高いことなどが要求される。かかる各種要求を満たす光情報記録層として、低融点で高い光吸収率を有し、熱伝導率が適当なTe被膜ないしTeを主成分とする被膜が知られているが、このTe系の被膜はその強い毒性が問題である。これに置き換わる低毒性，低融点の光情報記録層の材料として、BiやIn，Snなどもあるが，薄く連続した均一な膜が得られにくいためとか、熱伝導率がTeに比べて大きいとかの理由のために良好なピット形状が得られず，又、S/N比が低いなどという欠点，酸化され易く，高温高湿下での安定性が低く耐久性に劣るという欠点，機械的な強度が劣るという欠点などがある。これらの欠点を改良する方法として，Te，Bi，In，Snなど低融点金属膜をその両側からSiO_2膜などの酸化物膜で挟んでサンドイッチ構造にしたり，Te，Bi，In，Snなどをサーメット化した膜にしたりすることが提案されている。しかしながら，いずれの改善方法もピット形状，耐久性の点で不充分である。

本発明は，かかる点を改良し，更に一層優れた書き込み特性と耐久性を有する光情報記録担体を提供することを目的として研究の結果発明されたものであり，その要旨はレーザー光を照射して蒸発，気化あるいは化学反応により情報の記録が行なえる情報記録層が基体上に形成されてなる光情報記録担体において，上記情報記録材料層が金属と酸化物の複合層からなり，該情報記録材料層の少なくとも一方の面に炭素層，シリコン層，又はボロン層よりなる高融点金属または半金属又は半導体層（これらを本発

明において高融点半金属層という）が形成されている事を特徴とする光情報記録担体に関するものである。

以下、本発明を図面を参照しながら更に詳細に説明する。

本発明における光情報記録担体5の基体1としては、透過光読み取りの場合には透明ガラス板，ポリメチルメタクリレート，ポリエチレンテレフタレート，ポリプロピレン，ポリカーボネート，ポリ塩化ビニル，ポリアミド，ポリスチレンなどのポリマー、又はこれらの種々変成したポリマー，コポリマー，ブレンド物などのシートあるいはフィルムなどが使用され、又、反射光読み取りの場合には、反射コートを施した上記各種基板の他，アルミ板，アルミ合金板などが使用される。

かかる基体1上には情報記録材料層2と高融点半金属層3とを所定層有する光情報記録構成層4が形成されている。この情報記録材料層2としては金属と酸化物の複合層が使用される。この複合層の酸化物としては、いくつかの異なった酸化状態が存在し得るSnO_2，Fe_2O_3，Sb_2O_5，MnO_2，V_2O_5、又はこれらの少なくとも2種以上を組合せたもの，又はこれらの金属酸化物を1種以上含むものが使用できる。又、上記複合層の金属としては、特にレーザー光の吸収能を持たせるという点で、Cr，Mg，Ti，Zr，V，Nb，Ta，Mo，W，Mn，Fe，Co，Ni，Cu，Ag，Au，Zn，Al，In，Sn，Pb，Sb及びBiからなる金属の中から選ばれた1つの金属，又は上記金属の少なくとも1つ以上を含む合金が使用できる。本発明においては情報記録材料層2の少なくとも一方の面にC(炭素）層，Si（シリコン）層，又，B(ボロン）層より選ばれる高融点半金属層3が形成される。本発明における光情報記録構成層4のピット形成機構としては、第3図に示したレーザー光の照射によって酸化物層が他の酸化状態に変化し、その際発生されるガスによって高融点半金属層が塑性変形を起すという現象が主である。当然ながら記録層に若干の変化が起きている可能性があるが、少なくとも現在の書込パワーレベル（~10mW）では副次的変化である。

よって複合層を形成する金属としても、単に吸収を助けるだけでなく、反応にある程度寄与し、又金属自体が溶融気化を起こしにくいような比較的高融点のものが望ましい。その意味で、上記金属の中ではCr，Mg，Ti，Zr，V，Mn，Fe，Co，Ni，Cu，Alが良好で、中でも耐久性の面でCrが優れている。又，高融点半金属層としてC，Si，Bを選択した理由は、高融点なので，情報記録材料層2との相互作用が酸化物などに比べて小さく、変形を起こし易いと考えられたからである。その他に本発明における光情報記録構成層には以下の特徴がある。

(a) 高融点半金属層の厚さを適当な範囲に選べば、その反射防止効果により、レーザー波長での光情報記録構成層の反射率を低減させることができ、それによって書き込み感度を大巾に向上させることができる。

(b) レーザー照射によってガスを発生させる物質として、他に有機物が考えられるが、本発明のように酸化物を使用した方が長期的な耐久性で優れている。又、本発明のようにすべて無機物で構成した方が生産過程も簡便化できコスト上有利である。

(c) Cr，Ti，Zr，などの金属単体では、Teに比べて熱伝導率が大きく、書き込み感度も非常に低いが，酸化物と組み合せることにより、熱伝導率や熱容量の調整を行なうことができる。

本発明における情報記録材料層2の厚みは，レーザー書き込みにおける感度，記録部の大きさ，耐久性などから決定されるが，例えば20nm~400nm，好ましくは40nm~250nmの範囲が適当である。又、C，Si，B等の高融点半金属層3の厚みは、やはり感度，耐久性などから決定されるが、用いられるレーザーの波長によっても異なり、その波長での反射率がなるべく小さくなるような膜厚が選ばれる。その範囲は10nm~

200nm、好ましくは20nm～600nmの範囲が適当である。従って、情報記録材料層2と高融点半金属層3とが組み合わされた光情報記録構成層4の厚みは30nm～800nm、好ましくは60nm～350nmの範囲が適当である。

本発明における情報記録材料層2は、第4図に示したように酸化物中に金属を分散させた形態の複合層にしても良いし、又、第5図に示したように酸化物層と金属層の厚みをそれぞれ0.5nm～50nmにして、多層膜化してなる形態の複合層にしてもよい。なお、後者の場合、書き込み特性には、ほとんど影響を及ぼさない。又、後者の方がそれぞれの蒸発源を独自にコントロールでき、生産上有利である。

本発明においては、第1図に示したように情報記録材料層3の上に単に高融点半金属層3を積層した2層構成の光情報記録構成層4にしてもよいし、又、第2図に示すように情報記録材料層2を高融点半金属層3によりサンドイッチ構造状に挟んだ3層構成の光情報記録構成層4であってもよい。さらに、本発明において光情報記録構成層4を3層にした場合、情報記録材料層2をその両側から挟む高融点半金属層3としては、膜形成面から、同種材料とすることが好ましいが、情報記録材料層2の両側の高融点半金属層3を上記した当該材料の範囲内で異なる材料とすることもできる。又、本発明においては、光情報記録構成層4の上層若しくは下層に、又は基体の光情報記録構成層4の形成された面と反対面に、反射層、絶縁層、保護層、アンダーコート層、アルカリバリアー層、その他各種機能層を1層、ないし数層、あるいは組み合わせて形成することもできる。例えば、光情報記録担体の書き込み前後の反射率変化を増加させるために、

高融点半金属層／記録材料層／高融点半金属層／熱絶縁層／反射層／基体（例えば、C層／CrとSnO₂の複合層／C層／熱絶縁層／Al層／基体）

の様な5層の層構成を有する光情報記録担体として、光情報記録構成層側から書き込み、読み出しをすることも可能である。又、基体側からの書き込み、読み出しを行なうために、

反射層／熱絶縁層／高融点半金属層／記録材料層／高融点半金属層／基体（例えば、Al層／熱絶縁層／C層／CrとSnO₂の複合層／C層／基体）

の様な5層の構成を有する光情報記録担体とすることもできる。

本発明において、情報記録層及び高融点半金属層を基体上に形成する方法としては、特に限定されるものではなく、各種真空蒸着法、各種スパッタリング法、各種イオンプレーティング法など種々の被膜形成方法が利用できる。

以下、本発明の実施例について説明する。

実施例1

表面平滑性に優れている円形フロートガラス基体（直径：85mm、板厚：2mm）を用意し、酸化セリウムで表面を研摩した後、市販の中性洗剤でガーゼ洗浄し、水道水、蒸留水、エタノールの順で濯ぎを充分に行ない、窒素乾燥させた。この基体10を第6図に示したスパッター装置11内の回転する基体支持部材12に取り付けた。スパッター・ターゲットとしては、ステンレス製の皿に入れたカーボンのターゲット13，18、ステンレス製の皿に入れたクロムのターゲット15と、ステンレス製の皿に入れた酸化スズのターゲット16を用いた、各層の形成にあたっては、まず基体支持部12をシャッター14の上にセットし、真空槽15内を10^{-7} Torr台まで排気し、その後、高純度アルゴンガスを導入し、3×10^{-3} Torrの圧力にコントロールした。Cを充分にプレスパッターした後、基体10を回転させながらシャッター14を開き、コーテングを開始した。ターゲット13に印加する電力はC層の厚みが200Å程度になるように調整した。次に基体支持部12をシャッター17に上に移動、CrとSnO₂を充分にプレスした後、基体10を回転させながらシャッター17を開き、CrとSnO₂を交互に何層にも積層させた。ターゲット15，16に印加する電

力はCr層の1層の厚みが10Å程度、SnO_2層の1層の厚みが20Å程度になるように調整した。最後に基体支持部12をシャッター19の上に移動し、最初と同様にCを充分プレスパッターした後、基体10を回転させながらシャッター19を開き、コーティングを行なった。ターゲット18に印加する電力はC層の厚みがやはり200Å程度になるように調整した。この様にして得られた3層構成膜(C/CrとSnO_2複合膜/C)の全体の厚みは2000Å、He-Neの波長付近における反射率は23%、吸収率は69%であった。この光情報記録担体にHe-Neレーザーで書き込み評価を行なったところ、形状が良好の記録パターンが得られた(書き込みパワー8mW)。又、このサンプルを60℃95%RHの高温多湿雰囲気中に1週間放置しても、全く変化は認められず、分光特性もほとんど変化しなかった。

実施例2

実施例1と同様に基体10を洗浄・乾燥し、実施例1と同様にC/CrとSnO_2の複合膜/Cの3層構成膜を作成した。但し、両側のC層をつける際に印加する電力は実施例1の場合と全く同じにし、コーティング時間を半分にしてC層の厚みが100Å程度になるようにした。この様にして得られた3層構成膜の全体の厚みは1825Å、He-Neの波長付近における反射率は28%、吸収率は60%であった。この光情報記録担体にHe-Neレーザーで書き込み評価を行なったところ、形状が良好の記録パターンが得られた(書き込みパワー8mW)。又、このサンプルを60℃95%RHの高温多湿雰囲気中に1週間放置しても、全く変化は認められず、分光特性もほとんど変化しなかった。

実施例3

実施例1と同様に基体10を洗浄・乾燥し、基体支持部12に取り付け、この基体支持部12をシャッター17の上にセットし、真空槽15内を10^{-7} Torr台まで排気し、その後高純度アルゴンガスを導入し、3×10^{-3} Torrの圧力にコントロールした。CrとSnO_2を充分にプレスパッターした後、基体10を回転させながらシャッター17を開き、CrとSnO_2を交互に何層にも積層させた。ターゲット15，16に印加する電力はCr層の1層の厚みが10Å程度、SnO_2層の1層の厚みが20Å程度になるように調整した。次に基体支持部12をシャッター19の上に移動し、Cを充分にプレスパッターした後、基体10を回転させながらシャッター19を開き、コーティングを行なった。ターゲット18に印加する電力はC層の厚みが200Å程度になるように調整した。この様にして得られた2層構成膜の全体の厚みは1935Å、He-Neの波長付近における反射率は22%、吸収率は74%であった。この光情報記録担体に実施例1と同様に書き込み評価を行なった所、良好の記録パターンが得られ、60℃85%RHの高温多湿雰囲気中に1週間放置しても、全く変化は認められなかった。

実施例4

CrのターゲットのかわりにZrのターゲットを用い、実施例1と全同じ手順に従って3層構成膜(C/ZrとSnO_2の複合層/C)を作成した。膜の全体の厚みは、2375ÅでHe-Neの波長付近における反射率は18%、吸収率は81%であった。この光情報記録担体に実施例1，2，3と同様に書き込み評価を行なった所、良好の記録パターンが得られ、耐久性もほとんど問題なかった。

実施例1～4で得られた試料のテストの結果を表1に示す。

表 1

		吸収率 (He-Neレーザー波長付近)	記録パターン形状(書き込みパワー-8mW)	耐久性 (60℃95%RH 1週間)
1	実施例1により得られるサンプル	69%	良好	変化なし
2	実施例2により得られるサンプル	60%	良好	変化なし
3	実施例3により得られるサンプル	74%	良好	変化なし
4	実施例4により得られるサンプル	81%	良好	変化なし
5	比較例(Te単層)(厚さ:70nm)	45%	良好	変化あり

以上の様に、本発明の光情報記録担体は、レーザー光の照射時の光情報記録構成層の光吸収率が高く、書き込みに要するエネルギーが小さく、又書き込みが容易であり、記録パターン形状も良好で、耐久性も優れており、毒性もないという優れた利点を持っている。

4.図面の簡単な説明

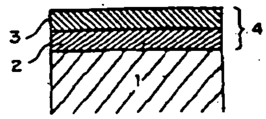
第1～3図は、本発明に係る光情報記録担体の一部横断面図を示したものであり、第4、5図は本発明に係る光情報記録担体の情報記録材料層の一部横断面図を示したものであり、第6図は本発明に係る光情報記録担体を製造するための装置の概略図である。

1：基体，　2：情報記録材料層，

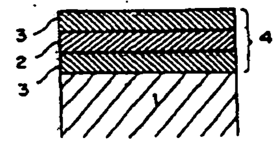
3：高融点半金属層，4：光情報記録構成層，

5：光情報記録担体

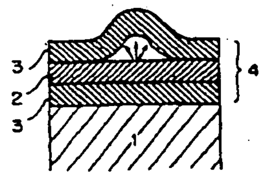
代理人　元橋賢治外1名



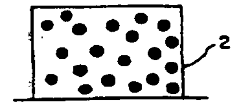
第1図



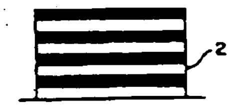
第2図



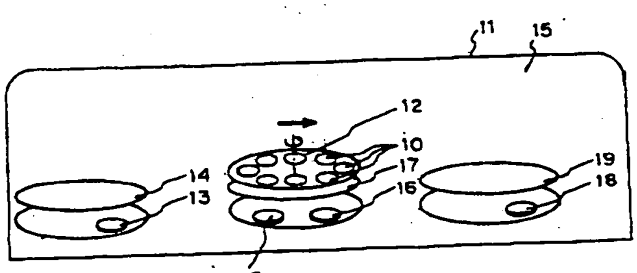
第3図



第4図



第5図



第6図